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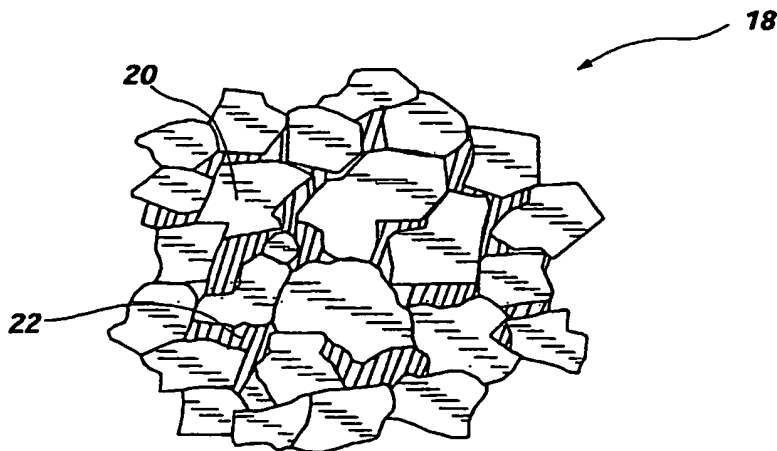
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(54) Title: **CONSOLIDATED HARD MATERIALS, METHODS OF MANUFACTURE, AND APPLICATIONS**



(57) Abstract: The present invention includes consolidated hard materials, methods for producing them, and industrial drilling and cutting applications for them. A consolidated hard material may be produced using hard particles such as  $B_4C$  or carbides or borides of W, Ti, Mo, Nb, V, Hf, Ta, Zr, and Cr in combination with an iron-based, nickel-based, nickel and iron-based, iron and cobalt-based, aluminum-based, copper-based, magnesium-based, or titanium-based alloy for the binder material. Commercially pure elements such as aluminum, copper, magnesium, titanium, iron, or nickel may also be used for the binder material. The mixture of the hard particles and the

binder material may be consolidated at a temperature below the liquidus temperature of the binder material using a technique such as rapid omnidirectional compaction (ROC), the Ceracon™ process, or hot isostatic pressing (HIP). After sintering, the consolidated hard material may be treated to alter its material properties.

WO 03/049889 A2

As alluded to above, in conventional liquid phase sintered tungsten carbide materials, as with many materials, fracture toughness is generally inversely proportional to hardness, while wear resistance is generally directly proportional to hardness. Although improvements in the fracture toughness of cemented tungsten carbide materials have been made over time, this parameter is still a limiting factor in many industrial applications where the cemented tungsten carbide structures are subjected to high loads during use. The material properties of cemented tungsten carbide can be adjusted to a certain degree by controlling the amount of cobalt binder, the carbon content, and the tungsten carbide grain size distribution.

5 However, the bulk of the advancements using these conventional metallurgical techniques have largely been realized. U.S. Patent 5,880,382 to Fang et al. attempts to solve some of the limitations of conventional WC-Co materials but uses expensive double cemented carbides.

Another drawback to conventional cemented-tungsten carbide materials is the limitation of using cobalt as the binder. About forty-five percent of the world's primary cobalt production is located in politically unstable regions, rendering supplies unreliable and requiring manufacturers to stockpile the material against potential shortfalls. Also, about fifteen percent of the world's annual primary cobalt market is used in the manufacture of cemented tungsten carbide materials. A large percentage of the cobalt supply is used in the production of superalloys used in aircraft engines, a relatively price-insensitive application which maintains fairly robust levels of cobalt prices. These factors contribute to the high cost of cobalt and its erratic price fluctuations.

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Cobalt has also been implicated as a contributor to heat checking when used as inserts in rolling cutter bits as well as in tungsten carbide substrates for cutters or cutting elements using superabrasive tables, commonly termed polycrystalline diamond compact (PDC) cutters. Heat checking, or thermal fatigue, is a phenomenon where the cemented tungsten carbide in either application rubs a formation, usually resulting in significant wear, and the development of fractures on the worn surface. It is currently believed that thermal cycling caused by frictional heating of the cemented tungsten carbide as it comes in contact with the formation,

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material according to the present invention may be produced using hard particles such as tungsten carbide and a binder material. The binder material may be selected from a variety of different aluminum-based, copper-based, magnesium-based, titanium-based, iron-based, nickel-based, iron and nickel-based, and iron and cobalt-based alloys. The binder may also be selected from commercially pure elements such as aluminum, copper, magnesium, titanium, iron, and nickel. Exemplary materials for the binder material may include carbon steels, alloy steels, stainless steels, tool steels, Hadfield manganese steels, nickel or cobalt superalloys, and low thermal expansion alloys. The binder material may be produced by mechanical alloying such as in an attritor mill or by conventional melt and atomization processing. The hard particles and the binder material may be mixed using an attritor or ball milling process. The mixture of the hard particles and binder material may be consolidated at a temperature below the liquidus temperature of the binder particles in order to prevent the formation of undesirable brittle carbides such as the double metal carbides commonly known as eta phase. It is currently preferred that the consolidation be carried out under at least substantially isostatic pressure applied through a pressure transmission medium. Commercially available processes such as Rapid Omnidirectional Compaction (ROC), the Ceracon™ process, or hot isostatic pressing (HIP) may be adapted for use in forming consolidated hard materials according to the present invention.

In an exemplary embodiment, at least one material characteristic of the binder, such as fracture toughness, strength, hardness, hardenability, wear resistance, thermo-mechanical characteristics (e.g. CTE, thermal conductivity), chemical characteristics (e.g. corrosion resistance, oxidation resistance), magnetic characteristics (e.g., ferromagnetism), among other material characteristics, may remain substantially the same before and after consolidation. Stated another way, binder material characteristics may not be significantly changed after the compacting or consolidation process. Stated yet another way, one or more binder material characteristics exhibited in a macrostructural or bulk state manifest themselves to at least a substantial extent in the consolidated hard material.

FIG. 4A and 4B illustrate the effect of heat treatments on several exemplary tungsten carbide materials of the present invention manufactured by subliquidus consolidation.

FIG. 5 is a graph of the Palmqvist crack resistance versus Vicker's hardness  
5 for several exemplary tungsten carbide materials of the present invention manufactured by subliquidus consolidation.

FIG. 6A-6G is x-ray diffraction patterns for several example tungsten carbide materials of the present invention manufactured by subliquidus consolidation.

FIG. 7 is a schematic view of a consolidated hard material insert according to  
10 the present invention.

FIG. 8 is a perspective view of a roller cone drill bit comprising a number of inserts according to the present invention as depicted in FIG. 7.

FIG. 9 is a perspective side view of a percussion or hammer bit comprising a number of inserts according to the present invention.

FIG. 10 is a perspective side view of a superabrasive shear cutter comprising  
15 a substrate formed from a consolidated hard material according to the present invention.

FIG. 11 is a perspective side view of a drag bit comprising a number of the superabrasive shear cutters configured as depicted in FIG. 10.

FIG. 12A is a perspective view of a drill bit carrying a nozzle formed at least  
20 in part from a consolidated hard material according to the present invention.

FIG. 12B is a sectional view of the nozzle depicted in FIG. 12A.

#### BEST MODES FOR CARRYING OUT THE INVENTION

Referring to FIG. 1, an exemplary microstructure of consolidated hard  
25 material 18 prepared according to the present invention is shown. FIG. 1 shows hard particles 20 bonded by binder material 22. In another exemplary embodiment for consolidated hard material 18, substantially all of hard particles 20 may be surrounded by a continuous binder material 22.

30 Exemplary materials for hard particles 20 are carbides, borides including boron carbide ( $B_4C$ ), nitrides and oxides. More specific exemplary materials for

include austenitic steels, nickel based superalloys such as INCONEL® 625M or Rene 95, and INVAR® type alloys with a coefficient of thermal expansion of about  $4 \times 10^{-6}$ , closely matching that of a hard particle material such as WC. More closely matching the coefficient of thermal expansion of binder material 22 with that of hard particles 20 offers advantages such as reducing residual stresses and thermal fatigue problems. Another exemplary material for binder material 22 is a Hadfield austenitic manganese steel (Fe with approximately 12 wt % Mn and 1.1 wt % C) because of its beneficial air hardening and work hardening characteristics.

Subliquidus consolidated materials according to the present invention may be prepared by using adaptations of a number of different methods known to one of ordinary skill in the art such as Rapid Omnidirectional Compaction (ROC) process, the Ceracon™ process, or hot isostatic pressing (HIP).

Broadly, and by way of example only, processing materials using the ROC process involves forming a mixture of hard particles and binder material, along with a fugitive binder to permit formation by pressing of a structural shape from the hard particles and binder material. The mixture is pressed in a die to a desired "green" structural shape. The resulting green insert is dewaxed and presintered at a relatively low temperature. The presintering is conducted to only a sufficient degree to develop sufficient strength to permit handling of the insert. The resulting "brown" insert is then wrapped in a material such as graphite foil to seal the brown insert. It is then placed in a container made of a high temperature, self-sealing material. The container is filled with glass particles and the brown parts wrapped in the graphite foil are embedded within the glass particles. The glass has a substantially lower melting temperature than that of the brown part or the die. Materials other than glass and having the requisite lower melting temperature may also be used as the pressure transmission medium. The container is heated to the desired consolidation temperature, which is above the melting temperature of the glass. The heated container with the molten glass and the brown parts immersed inside is placed in a mechanical or hydraulic press, such as a forging press, that can apply sufficient loads to generate isostatic pressures to fully consolidate the brown part. The molten glass acts to transmit the load applied by the press uniformly to the

As the process continues, particles become increasingly comprised of a homogenous mixture of the constituent powders in the same proportion in which they were mixed.

To form the mechanically alloyed binder finely divided particles of iron based alloys, nickel based alloys, iron and nickel based alloys and iron and cobalt based alloys, and carbon in the form of lamp black or finely divided graphite particles may be disposed in the attritor mill and milling initiated until a desired degree of alloying is complete. It should be noted that complete alloying may be unnecessary, as a substantially mechanically alloyed composition may complete the alloying process during subsequent consolidation to form the material of the present invention.

Alternatively, binder material 22 may be alloyed by conventional melting processes and then atomized into a fine particulate state as is known to those of ordinary skill in the art. In yet another exemplary implementation, binder material 22 may become substantially mechanically alloyed, and then complete some portion of alloying during the sintering process.

In an exemplary embodiment, one or more material characteristics of binder material 22 such as fracture toughness, strength, hardness, hardenability, wear resistance, thermo-mechanical properties (e.g. CTE, thermal conductivity), chemical properties (e.g. corrosion resistance, oxidation resistance), and magnetic properties (e.g. ferromagnetism), among others, may be substantially unaffected upon consolidation with hard particles 20. In other words, binder material 22 substantially retains one or more material characteristics possessed or exhibited prior to consolidation when it is in its cemented state with hard particles 20. Stating the material characteristics exhibited by the consolidated hard material 18 another way, at least one material characteristic exhibited by binder material 22 in a macrostructural state, manifests itself in the consolidated hard material 18. The term "macrostructural" is used in accordance with its common meaning as "[t]he general arrangement of crystals in a solid metal (e.g. an ingot) as seen by the naked eye or at low magnification. The term is also applied to the general distribution of impurities in a mass of metal as seen by the naked eye after certain methods of etching.",

pressing or shaping. Techniques for forming the green parts are well known to those of ordinary skill in the art.

The green part is then dewaxed by way of vacuum or flowing hydrogen at elevated temperature. Subsequent to dewaxing, the dewaxed green part is subjected to a partial sintering furnace cycle in order to develop sufficient handling strength. The now brown part is then wrapped in graphite foil, or otherwise enclosed in a suitable sealant or canning material. The wrapped, dewaxed brown part is then again heated and subjected to an isostatic pressure during a consolidation process in a medium such as molten glass to a temperature that is below the liquidus temperature of the phase diagram for the particular, selected binder material 22. It is subjected to elevated pressures, at the particular temperature sufficient to completely consolidate the material. Accordingly, such an exemplary embodiment of hard material 18 may be said to be subliquidus sintered. In accordance with the present invention, the consolidation temperature may be below the liquidus temperature of the binder material 22 and above the solidus temperature, or may be below both the liquidus and solidus temperatures of the binder material, as depicted on a phase diagram of the selected binder material 22. It is currently preferred that the sintering operation be conducted in an "incipient melting" temperature zone, where a small and substantially indeterminate portion of the binder material may experience melting, but the binder material as a whole remains in a solid state. Alternatively, sintering below the solidus temperature of the binder material 22 as depicted on the phase diagram may be used to practice the present invention.

By performing the consolidation process below the liquidus temperature of binder material 22, chemical alteration of the binder alloy may be minimized. Alterations of the binder are facilitated by the exposure of the binder in its liquid state to other materials where chemical reactions, diffusion, dissolution, and mixing are possible. Formation of undesirable brittle carbides in binder material 22, for example may be prevented when the subliquidus consolidation process is employed and the liquid state is avoided. As is known to those skilled in the art, examples of these undesirable brittle phases, also known as double metal carbides are,  $\text{FeW}_3\text{C}$ ,  $\text{Fe}_3\text{W}_3\text{C}$ ,  $\text{Fe}_6\text{W}_6\text{C}$ ,  $\text{Ni}_2\text{W}_4\text{C}$ ,  $\text{Co}_2\text{W}_4\text{C}$ ,  $\text{Co}_3\text{W}_3\text{C}$ , and  $\text{Co}_6\text{W}_6\text{C}$  which may develop

After subliquidus consolidation, the consolidated hard material of the present invention may be subjected to post consolidation thermal, chemical, or mechanical treatments to modify its material properties or characteristics. As an example, subsequent, to subliquidus consolidation, the part may be heat treated, such as by  
5 traditional annealing, quenching, tempering, or aging, as widely practiced by those of ordinary skill in the art with respect to metals and alloys but not with respect to cemented carbides or similar consolidated materials, to alter the properties or characteristics of the material as significantly affected by the response of binder material used therein.

10 Exemplary surface treatments that also may be used to increase the hardness of the surface of a consolidated hard material of the present invention are carburizing, carbonitriding, nitriding, induction heating, flame hardening, laser surface hardening, plasma surface treatments, and ion implantation. Exemplary mechanical surface hardening methods include shot peening and tumbling. Other  
15 surface treatments will be apparent to one of ordinary skill in the art.

The consolidated hard materials of this invention will be better understood with reference to the following examples shown in Table I, FIG. 2B and the descriptions below. FIG. 2B is a phase diagram which includes Alloys A through F of Examples 1 through 6 below, indicated by appropriate letters respectively  
20 corresponding to the examples. Note that the region to the right of line B-F does not contain graphite in the inventive process.



## EXAMPLE 2 - Alloy B

Binder material 22 was prepared according to the above attritor milling process. Approximately 75 wt % hard particles 20 and 25 wt % binder material 22 was used. Binder material 22 was comprised of 97.0 wt % Fe-3.0 wt % C. Binder material 22 was approximately 1  $\mu\text{m}$  in particle size. The hard particles 20 were WC approximately 6  $\mu\text{m}$  to 7  $\mu\text{m}$  in size. The mixture of hard particles 20 and binder material 22 was pressed into rectangular bars, dewaxed, and presintered at 500 °C in a methane atmosphere and then different samples were separately subjected to ROC processing at 1050 °C and 1100°C. After ROC processing at 1050 °C the resulting subliquidus consolidated tungsten carbide material had an average HRA of 82.9. After ROC processing at 1100 °C the resulting subliquidus consolidated tungsten carbide material had an average HRA of 81.1. By contrast, the same material processed conventionally by liquid phase sintering had an average HRA of 76.0. After austenitizing and oil quenching the subliquidus consolidated tungsten carbide material to room temperature, following ROC processing at 1050 °C, the resulting HRA was 85.0. After austenitizing and oil quenching the material to room temperature, following ROC processing at 1100 °C, the resulting average HRA was 83.2.

## EXAMPLE 3 - Alloy C

Binder material 22 was prepared according to the above attritor milling process. Approximately 75 wt % hard particles 20 and 25 wt % binder material 22 was used. Binder material 22 was comprised of 68.0 wt % Fe-32.0 wt % Ni. Binder material 22 was approximately 1  $\mu\text{m}$  in particle size. The hard particles 20 were WC approximately 6  $\mu\text{m}$  to 7  $\mu\text{m}$  in size. The mixture of hard particles 20 and binder material 22 was pressed into rectangular bars, dewaxed, and presintered at 500 °C in a methane atmosphere and then subjected to ROC processing at approximately 1225°C. After ROC processing the resulting subliquidus consolidated tungsten carbide material had an average HRA of 78.0. After reheating to approximately 900°C and oil quenching the material, following ROC processing, to room temperature, the resulting average HRA was 77.3. Subsequent quenching of

austenitizing and oil quenching to room temperature the ROC processed material had an average HRA of 81.9. Subsequent quenching of this sample in liquid nitrogen resulted in an average HRA of 85.8.

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#### EXAMPLE 5 - Alloy E

Binder material 22 was prepared according to the above attritor milling process. Approximately 75 wt % hard particles 20 and 25 wt % binder material 22 was used. Binder material was comprised of 98.6 wt % Fe-1.4 wt % C. Binder material 22 was approximately 1  $\mu$ m in particle size. The hard particles 20 were WC approximately 6  $\mu$ m to 7  $\mu$ m in size. The mixture of hard particles 20 and binder material 22 was pressed into rectangular bars, dewaxed, and presintered at 500 °C in a methane atmosphere and then samples were separately subjected to ROC processing at approximately 1050 °C and 1100°C. After ROC processing at 1050 °C the resulting subliquidus consolidated tungsten carbide material had an average HRA of 80.2. After ROC processing at 1100 °C the resulting subliquidus consolidated tungsten carbide material had an average HRA of 80.1. Subsequent austenitizing and oil quenching the material to room temperature, following ROC processing at 1050 °C, resulted in an average HRA of 83.8. Subsequent austenitizing and oil quenching the material to room temperature, following ROC processing at 1100 °C, resulted in an average HRA of 83.5. The same material processed conventionally by liquid phase sintering had an average HRA of 79.2.

#### EXAMPLE 6 - Alloy F

Binder material 22 was prepared according to the above attritor milling process. Approximately 75 wt % hard particles 20 and 25 wt % binder material 22 was used. Binder material was comprised of 79.2 wt % Fe-19.8 wt % Ni-1.0 wt % C. Binder material 22 was approximately 1  $\mu$ m in particle size. The hard particles 20 were WC approximately 6  $\mu$ m to 7  $\mu$ m in size. The mixture of hard particles 20 and binder material 22 was pressed into rectangular bars, dewaxed, and presintered at 500 °C in a methane atmosphere and then subjected to ROC processing at approximately 1150°C. After ROC processing, the resulting subliquidus

solution may be any metal, but is usually aluminum, niobium, or titanium. The gamma" phase is typically identified as  $\text{Ni}_3(\text{Nb}, \text{Ti}, \text{Al})$  and most commonly as  $\text{Ni}_3\text{Nb}$ . Another intermetallic compound, also used to precipitation strengthen superalloys, with the same stoichiometry but different crystal structure, is a gamma' phase that may be identified as  $\text{M}_3\text{Al}$  (i.e.  $\text{Ni}_3\text{Al}$ ,  $\text{Ti}_3\text{Al}$ , or  $\text{Fe}_3\text{Al}$ ).

Referring to FIGs. 4A and 4B, the effect of heat treatments on the subliquidus consolidated tungsten carbide materials formulated with the exemplary alloy binder compositions is shown. FIG. 4A shows that alloy B, C, and E gain toughness with little change in hardness as a result of solution treatment followed by quenching. FIG. 4B shows that alloys A, D, and F undergo an increase in hardness accompanied by a drop in toughness as a result of solution treatment followed by quenching. As shown in FIGs. 4A and 4B, the material properties of subliquidus consolidated tungsten carbide materials of the present invention may be altered by heat treating, in contrast with conventional cobalt cemented tungsten carbide materials.

Referring to FIG. 5, Palmqvist crack resistance versus Vickers hardness of the heat treated subliquidus consolidated tungsten carbide materials of the above examples compared to two conventional carbide grades (3255 and 2055) is shown. Grades 3255 and 2055 are common, commercially available, 16% and 10% cobalt respectively, carbide grades widely used in petroleum drill bits. As shown by FIG. 5, subliquidus consolidated materials of the present invention may exhibit hardness/toughness combinations more desirable than conventional carbide materials.

Referring to FIGs. 6A-6G, X-ray diffraction patterns of the above example subliquidus consolidated tungsten carbide materials are shown. The X-ray diffraction patterns are dominated by tungsten carbide since it makes up 75 wt % of the materials. FIGs. 6A-6G demonstrates that neither double metal carbides phases nor graphite (free carbon) are present in the subliquidus consolidated materials of the above examples. FIGs. 6A-6G further demonstrate that the phases expected from the starting compositions of the binder materials are present even upon subliquidus consolidation with the tungsten carbide hard particles.

example, with a drag bit for drilling subterranean formations. More specifically, consolidated hard materials of the present invention may be used to form a shear cutter substrate 44 that is used to carry a layer or "table" of polycrystalline diamond 46 that is formed on it at ultrahigh temperatures and pressures, the techniques for same being well known to those of ordinary skill in the art. It should be noted that conventional substrates of cobalt binder tungsten carbide may employ "sweeping" of cobalt from the substrate as a catalyst for the formation of the diamond table. Using a substrate of the present invention, one would add cobalt in or adjacent to the particulate diamond before pressing to form the diamond table to provide the catalyst. Referring to FIG. 11, an illustrated drag bit 48 includes a plurality of such PDC cutters 42 that are each attached to blades 50 that extend from a body 52 of the drag bit for cutting against the subterranean formation being drilled.

FIGs. 12A and 12B respectively illustrate a conventional roller cone drill bit 50 having a nozzle 52 and inserts 24 made from a consolidated hard material of the present invention and an enlarged cross-sectional view of a nozzle 52. Drill bit 50 has a central passage 56 therethrough and outlets 58 associated with each cone 32 (only one outlet shown). FIG. 12B shows nozzle 52 in more detail. The inner part of nozzle 52, or even the entire nozzle, comprises a nozzle insert 60 made from a consolidated hard material of this invention.

Although the foregoing description of consolidated hard materials, production methods, and various applications of them contain many specifics, these should not be construed as limiting the scope of the present invention, but merely as providing illustrations of some exemplary embodiments. Similarly, other embodiments of the invention may be devised which do not depart from the spirit or scope of the present invention. The scope of the invention is, therefore, indicated and limited only by the appended claims and their legal equivalents, rather than by the foregoing description. All additions, deletions, and modifications to the invention, as disclosed herein, which fall within the meaning and scope of the claims are to be embraced.

6. The consolidated hard material of claim 1, wherein the binder comprises about 3 to 50 weight percent and the plurality of hard particles comprises about 50 to 97 weight percent of the total weight of the consolidated hard material.

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7. The consolidated hard material of claim 1, wherein the binder comprises about 68 to 80 weight percent iron, about 19 to 32 weight percent nickel, and about 0 to 1.0 weight percent carbon.

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8. The consolidated hard material of claim 1, wherein the binder comprises about 88 to 99 weight percent iron, about 0 to 10 weight percent nickel, and about 0 to 3.0 weight percent carbon.

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9. The consolidated hard material of claim 1, wherein the binder comprises about 60.5 weight percent nickel, about 20.5 weight percent chromium, about 9.0 weight percent molybdenum, about 5.0 weight percent niobium, and about 5.0 weight percent iron.

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10. The consolidated hard material of claim 1, wherein the binder comprises a Hadfield austenitic manganese steel.

11. The consolidated hard material of claim 1, wherein the consolidated hard material is substantially free of double metal carbides.

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12. A consolidated hard material, comprising:  
a plurality of hard particles selected from  $B_4C$  and carbides or borides of the group consisting of W, Ti, Mo, Nb, V, Hf, Ta, Zr, and Cr; and  
a binder selected from the group consisting of iron-based alloys, nickel-based alloys, iron and nickel-based alloys, iron and cobalt-based alloys, aluminum-based alloys, copper-based alloys, magnesium-based alloys, titanium-based alloys,  
commercially pure aluminum, commercially pure copper, commercially pure

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19. The consolidated hard material of claim 12, wherein the binder comprises about 88 to 99 weight percent iron, about 0 to 10 weight percent nickel, and about 0 to less than 0.5 weight percent carbon.

5        20. The consolidated hard material of claim 12, wherein the binder comprises about 60.5 weight percent nickel, about 20.5 weight percent chromium, about 9.0 weight percent molybdenum, about 5.0 weight percent niobium, about 5.0 weight percent iron.

10        21. The consolidated hard material of claim 12, wherein the binder comprises a Hadfield austenitic manganese steel.

22. A method for making a consolidated hard material comprising:  
15        providing a binder including a material selected from the group consisting of iron-based alloys, nickel-based alloys, iron and nickel-based alloys, iron and cobalt-based alloys, aluminum-based alloys, copper-based alloys, magnesium-based alloys, and titanium-based alloys, commercially pure aluminum, commercially pure copper, commercially pure magnesium, commercially pure titanium, commercially pure iron and commercially pure  
20        nickel ;  
providing a plurality of hard particles selected from  $B_4C$  and carbides or borides of the group consisting of W, Ti, Mo, Nb, V, Hf, Ta, Zr, and Cr;  
forming a mixture of the binder and the plurality of hard particles;  
pressing the mixture of the binder and the plurality of hard particles into a shape;  
25        and  
sintering the pressed shape including the plurality of hard particles and the binder below a liquidus temperature of the binder.

23. The method of claim 22, wherein the consolidated hard material is  
30        consolidated below a liquidus temperature and above a solidus temperature of the binder.

32. The method of claim 22, further comprising providing the binder as about 3 to 50 weight percent and the plurality of hard particles as about 50 to 97 weight percent of the total weight of the consolidated hard material.

5           33. The method of claim 22, further comprising formulating the binder with about 68 to 80 weight percent iron, about 19 to 32 weight percent nickel, and about 0 to 1.0 weight percent carbon.

10           34. The method of claim 22, further comprising formulating the binder with a composition of about 88 to 99 weight percent iron, about 0 to 10 weight percent nickel, and about 0 to 3.0 weight percent carbon.

15           35. The method of claim 22, further comprising formulating the binder with a composition of about 60.5 weight percent nickel, about 20.5 weight percent chromium, about 9.0 weight percent molybdenum, about 5.0 weight percent niobium, and about 5.0 weight percent iron.

            36. The method of claim 22, further comprising formulating the binder with a Hadfield austenitic manganese steel.

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            37. The method of claim 22, further comprising at least partially coating the hard particles with the binder during the forming the mixture.

25           38. The method of claim 37, further comprising forming the mixture and at least partially coating the hard particles with the binder in an attritor mill.

            39. The method of claim 22, further comprising forming the binder by mechanical alloying.

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45. The method of claim 44, wherein the consolidated hard material is consolidated below a liquidus temperature of the binder.

5 46. The method of claim 44, wherein the consolidated hard material is consolidated below a liquidus temperature and above a solidus temperature of the binder.

10 47. The method of claim 44, wherein the consolidated hard material is subliquidus consolidated below a solidus temperature of the binder.

48. The method of claim 44, further comprising surrounding the body with a pressure transmission medium and applying pressure to the body therethrough during sintering.

15 49. The method of claim 44, wherein the sintering is performed while the pressed body is generally under isostatic pressure.

20 50. The method of claim 44, further comprising heat treating the consolidated hard material.

51. The method of claim 44, further comprising precipitation hardening the consolidated hard material.

25 52. The method of claim 44, further comprising forming the binder by mechanical alloying.

53. The method of claim 44, further comprising surface hardening the consolidated hard material.



61. The method of claim 60, further comprising forming the mixture and at least partially coating the hard particles with the binder in an attritor mill.

62. The method of claim 61, further comprising forming the binder by  
5 mechanical alloying.

63. The method of claim 62, further comprising effecting the mechanical alloying in an attritor mill.

10 64. The method of claim 63, further comprising at least partially coating the hard particles with the binder during the forming of the mixture.

65. The method of claim 64, further comprising forming the mixture and at least partially coating the hard particles with the binder in an attritor mill.

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66. The method of claim 65, wherein the binder is mechanically alloyed and the mixture of the binder and the hard particles is formed in the same attritor mill.

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67. A drill bit comprising:  
a body having a structure adapted to engage a subterranean formation during drilling;  
a plurality of inserts carried on the structure, the inserts formed from a consolidated hard material comprising:

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a plurality of hard particles selected from  $B_4C$  and carbides or borides of the group consisting of W, Ti, Mo, Nb, V, Hf, Ta, Zr, and Cr, and  
a binder including a material selected from the group consisting of iron-

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based alloys, nickel-based alloys, iron and nickel-based alloys, iron and cobalt-based alloys, aluminum-based alloys, copper-based alloys, magnesium-based alloys, and titanium-based alloys, commercially pure aluminum, commercially pure copper, commercially pure

74. The drill bit of claim 67, wherein the binder comprises about 88 to 99 weight percent iron, about 0 to 10 weight percent nickel, and about 0 to 3.0 weight percent carbon.

5           75. The drill bit of claim 67, wherein the binder comprises about 60.5 weight percent nickel, about 20.5 weight percent chromium, about 9.0 weight percent molybdenum, about 5.0 weight percent niobium, and about 5.0 weight percent iron.

10           76. The drill bit of claim 67, wherein the binder comprises a Hadfield austenitic manganese steel.

77. The drill bit of claim 67, wherein the consolidated hard material is substantially free of double metal carbides.

15

78. A superabrasive cutter, comprising:

a substrate formed from a consolidated hard material comprising:

a plurality of hard particles selected from  $B_4C$  and carbides or borides of the group consisting of W, Ti, Mo, Nb, V, Hf, Ta, and Cr; and

20           a binder including a material selected from the group consisting of iron-based alloys, nickel-based alloys, iron and nickel-based alloys, iron and cobalt-based alloys, aluminum-based alloys, copper-based alloys, magnesium-based alloys, and titanium-based alloys, commercially pure aluminum, commercially pure copper, commercially pure magnesium, commercially pure titanium, commercially pure iron, and commercially pure nickel, the binder cemented with the plurality of hard particles;

25

wherein the consolidated hard material exhibits at least one material characteristic selected from the group consisting of mechanical characteristics, thermo-mechanical characteristics, chemical characteristics, and magnetic characteristics exhibited by the binder

30

chemical characteristics, and magnetic characteristics exhibited by the binder in a macrostructural state.

82. A consolidated hard material comprising:

- 5 a plurality of hard particles selected from  $B_4C$  and carbides or borides of the group consisting of W, Ti, Mo, Nb, V, Hf, Ta, Zr, and Cr;  
a binder selected from the group consisting of iron-based alloys, nickel-based alloys, iron and nickel-based alloys, iron and cobalt-based alloys, aluminum-based alloys, copper-based alloys, magnesium-based alloys, and titanium-based  
10 alloys, commercially pure aluminum, commercially pure copper, commercially pure magnesium, commercially pure titanium, commercially pure iron and commercially pure nickel, the binder cemented with a plurality of hard particles;

wherein at least one material characteristic exhibited by the binder in a  
15 macrostructural state and selected from the group consisting of mechanical characteristics, thermo-mechanical characteristics, chemical characteristics, and magnetic characteristics is not substantially altered in the consolidated hard material.

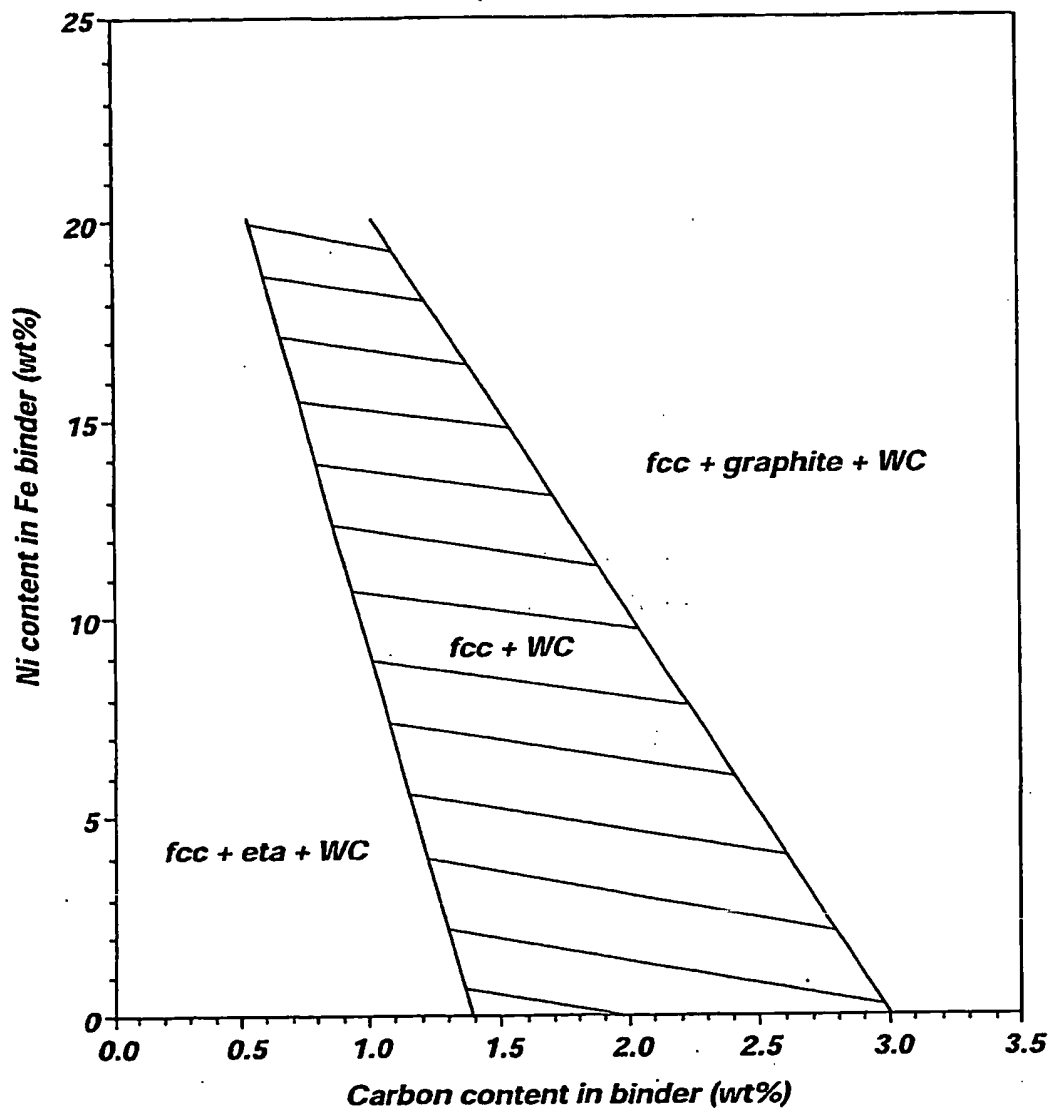
20 83. A consolidated hard material, comprising:

- a plurality of hard particles selected from  $B_4C$  and carbides or borides of the group consisting of W, Ti, Mo, Nb, V, Hf, Ta, Zr, and Cr cemented with a subliquidus transformed binder selected from the group consisting of iron-based alloys, nickel-based alloys, iron and nickel-based alloys, iron and cobalt-based alloys, aluminum-based alloys, copper-based alloys, magnesium-based alloys, and titanium-based  
25 alloys, commercially pure aluminum, commercially pure copper, commercially pure magnesium, commercially pure titanium, commercially pure iron and commercially pure nickel.

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2/15

**Phase regions of (Fe + Ni) + WC resulting  
from liquid phase sintering as a  
function of binder Carbon content  
(Moskowitz)**

**FIG. 2A**

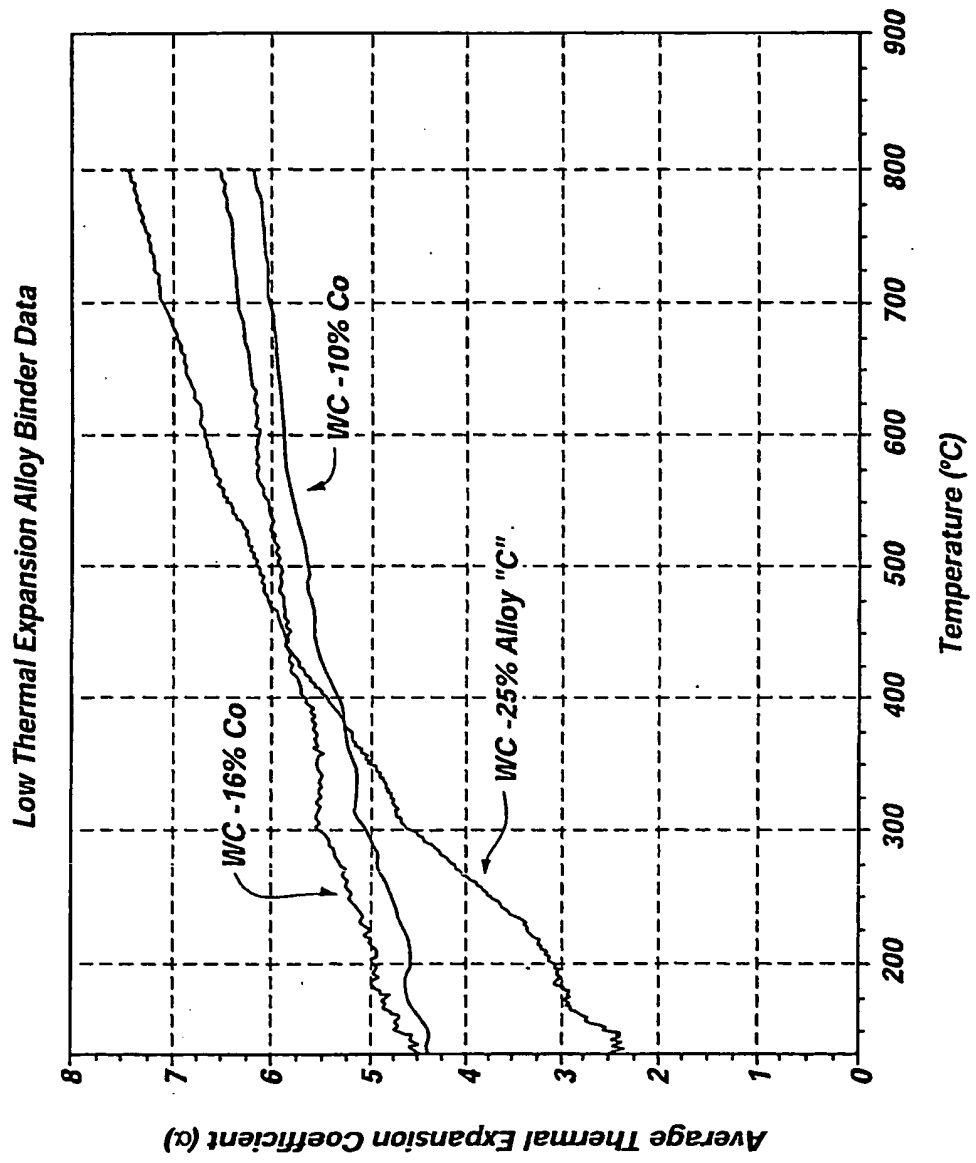
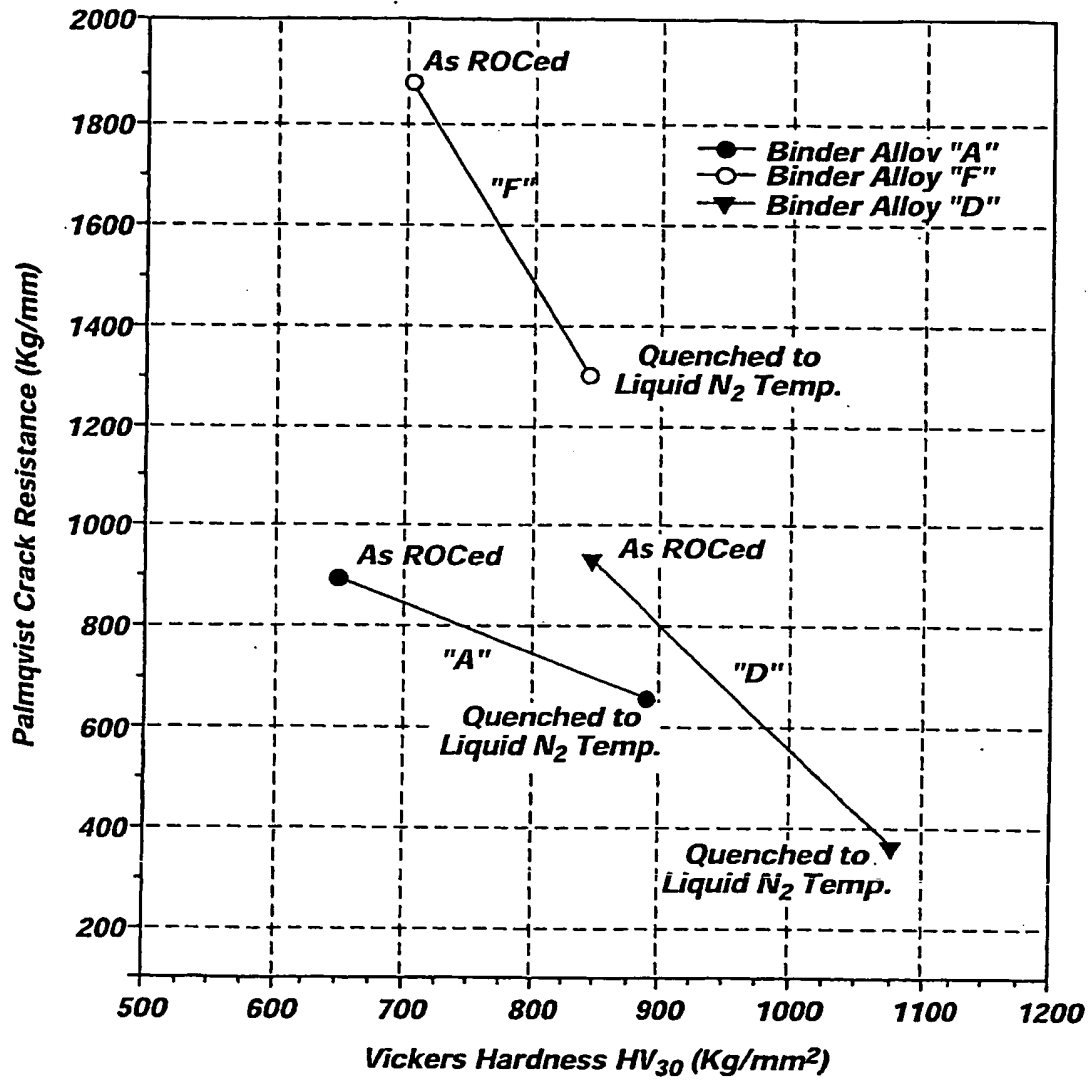


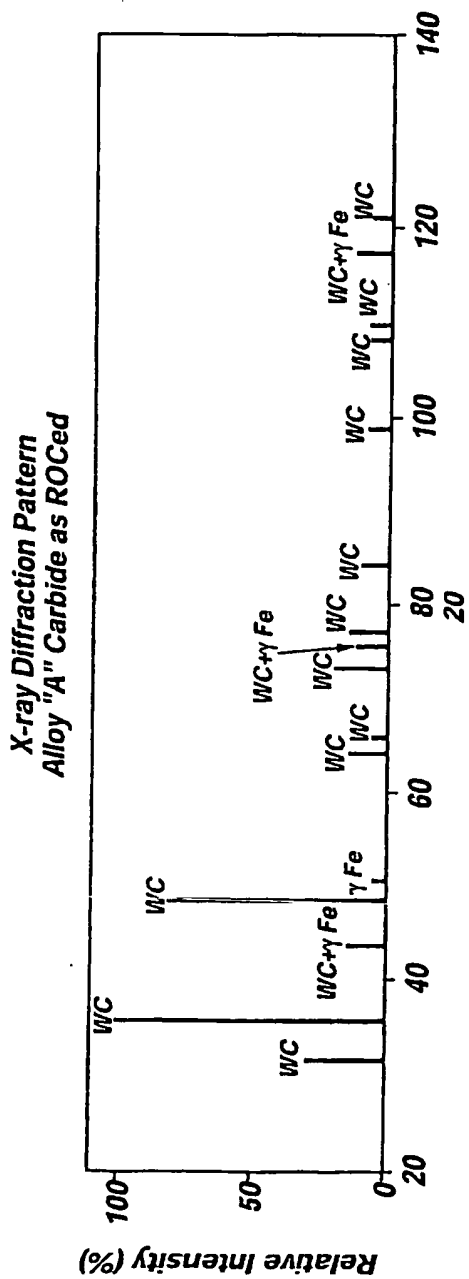
FIG. 3

6/15

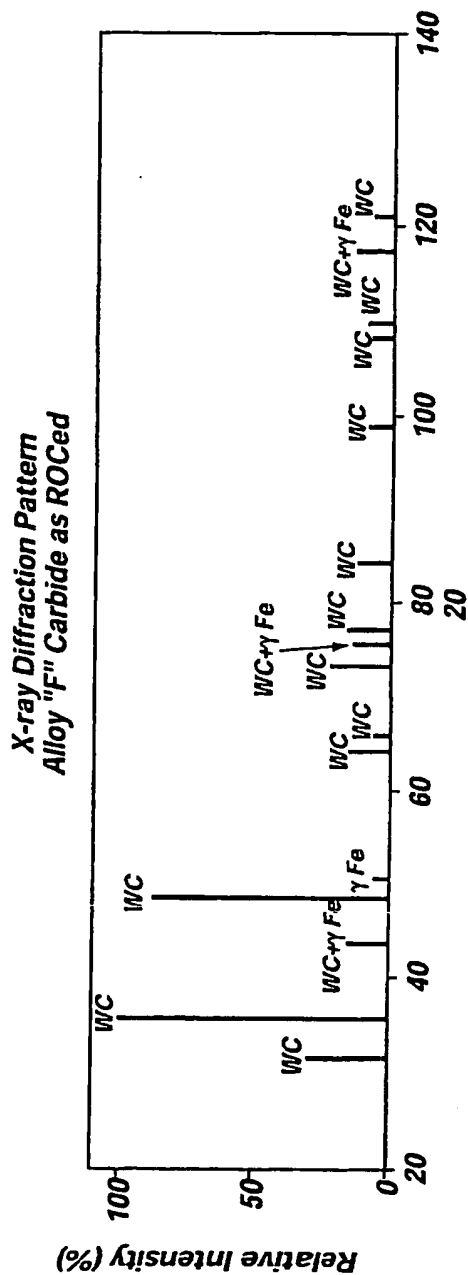
**Subliquidus Consolidated Alloy Binder Carbide  
Hardness/Toughness Curves**

**FIG. 4B**

8/15

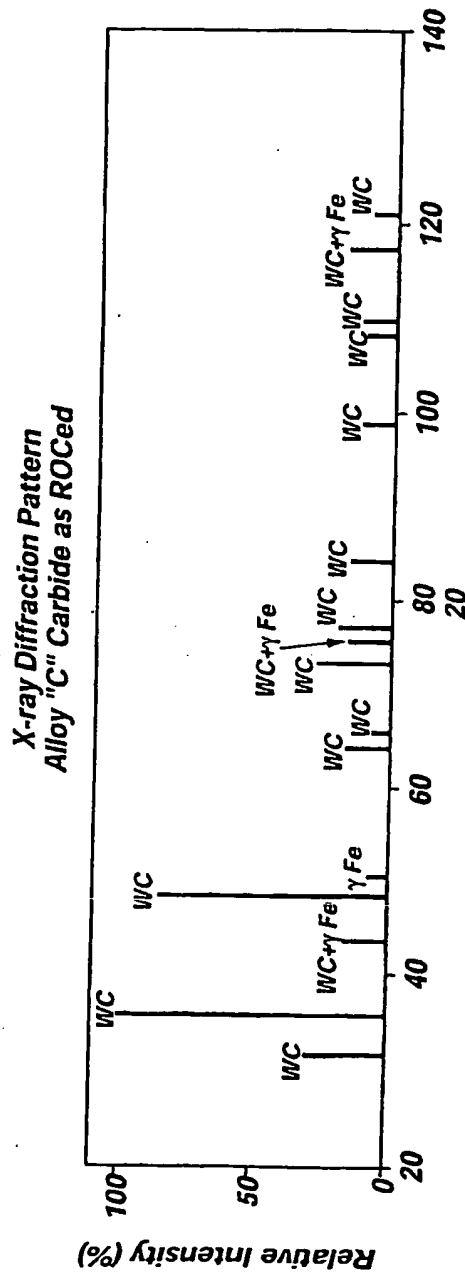
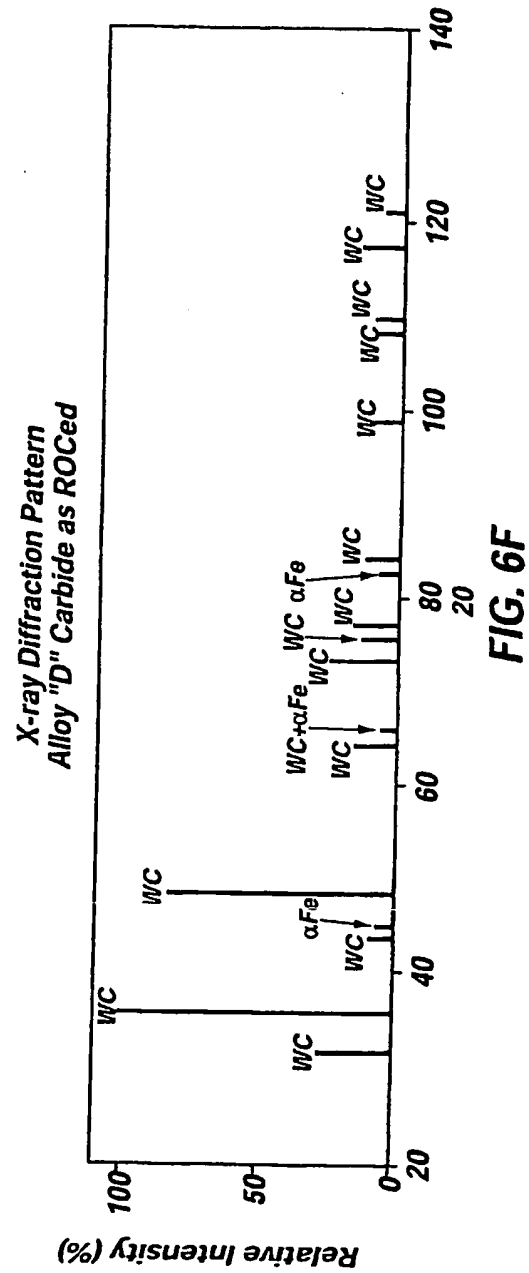


**FIG. 6A**



**FIG. 6B**

10/15

**FIG. 6E****FIG. 6F**



12/15

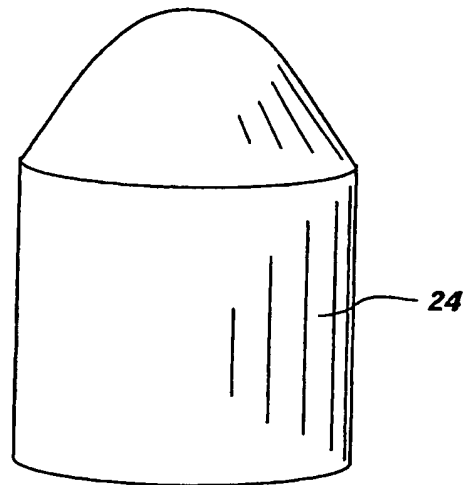


FIG. 7

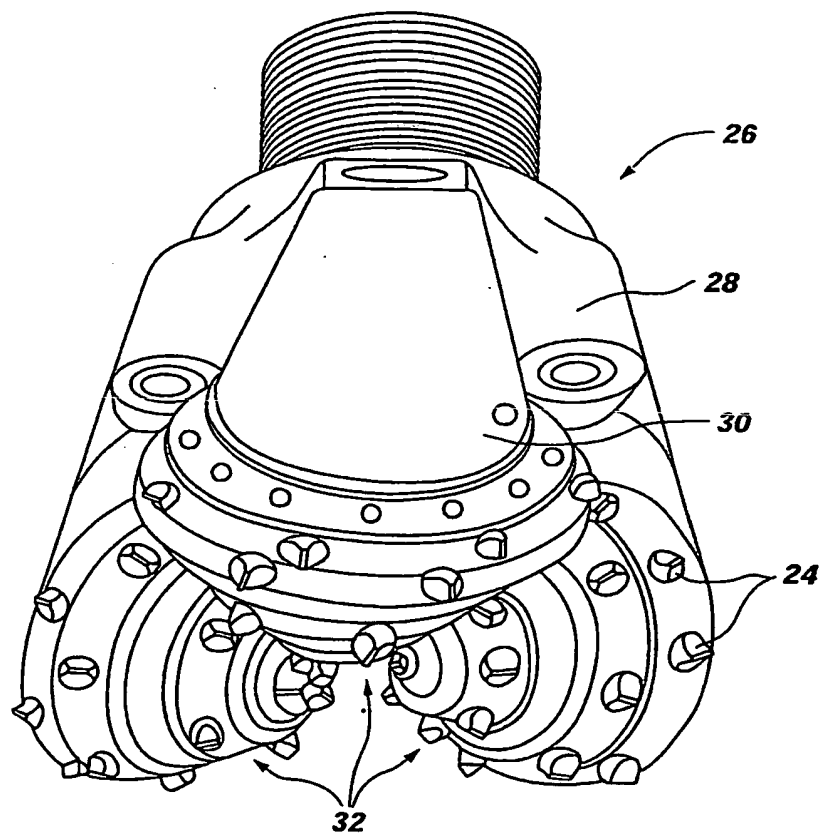


FIG. 8

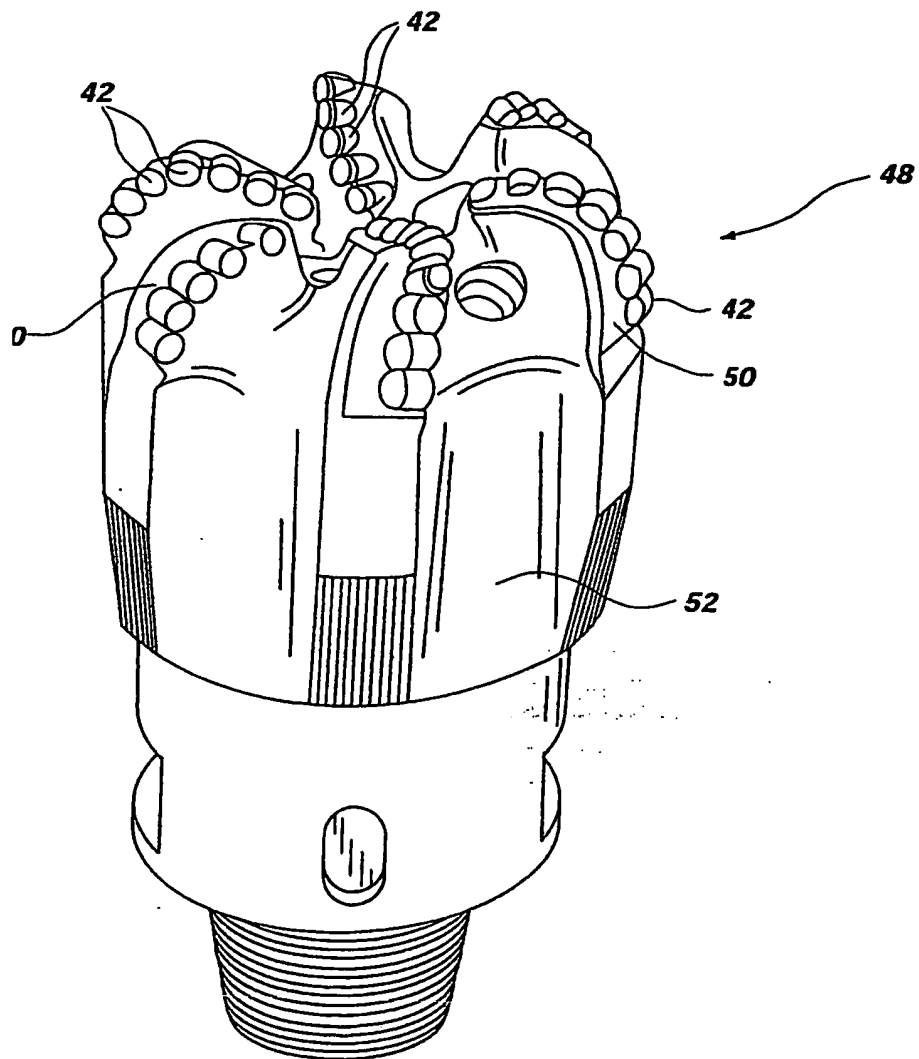


FIG. 11

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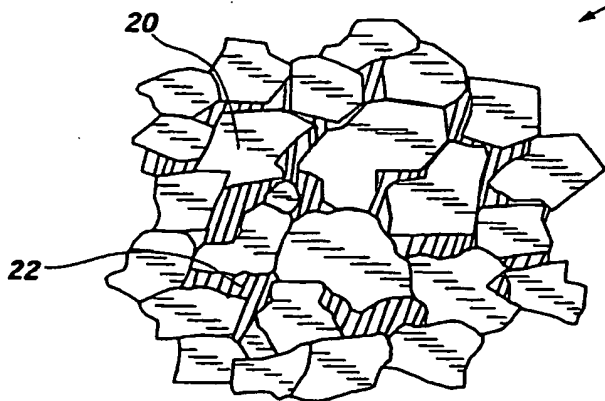
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(54) Title: CONSOLIDATED HARD MATERIALS, METHODS OF MANUFACTURE, AND APPLICATIONS



18

(57) Abstract: The present invention includes consolidated hard materials, methods for producing them, and industrial drilling and cutting applications for them. A consolidated hard material may be produced using hard particles such as B<sub>4</sub>C or carbides or borides of W, Ti, Mo, Nb, V, Hf, Ta, Zr, and Cr in combination with an iron-based, nickel-based, nickel and iron-based, iron and cobalt-based, aluminum-based, copper-based, magnesium-based, or titanium-based alloy for the binder material. Commercially pure elements such as aluminum, copper, magnesium, titanium, iron, or nickel may also be used for the binder material. The mixture of the hard particles and the binder material may be consolidated at a temperature

below the liquidus temperature of the binder material using a technique such as rapid omnidirectional compaction (ROC), the Ceracon™ process, or hot isostatic pressing (HIP). After sintering, the consolidated hard material may be treated to alter its material properties.

WO 03/049889 A3

# INTERNATIONAL SEARCH REPORT

PCT/US02/38664

## C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,973,356 A (VON HOLST et al.) 27 November 1990 (27.11.1990)	
A	US 5,015,290 A (TIEGS et al.) 14 May 1991 (14.05.1991)	
A	US 5,223,020 A (KOLASKA) 29 June 1993 (29.06.1993)	
A	US 5,570,750 A (WILLIAMS) 05 November 1996 (05.11.1996)	
A	US 6,248,150 B1 (AMICK) 19 June 2001 (19.06.2001)	

Form PCT/ISA/210 (second sheet) (July 1998)

# INTERNATIONAL SEARCH REPORT

PCT/US02/38664

## BOX II. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This application contains claims directed to more than one species of the generic invention. These species are deemed to lack unity of invention because they are not so linked as to form a single general inventive concept under PCT Rule 13.1.

In order for more than one species to be examined, the appropriate additional examination fees must be paid. The species are as follows:

- a) binder comprises about 68 to 80 wt. % Fe, about 19-32 wt. % Ni, and about 0 to 1.0 wt. % C,
- b) binder comprises about 88 to 99 wt. % Fe, about 0 to 10 wt. % Ni, and about 0 to 3.0 wt. % C,
- c) binder comprises about 60.5 wt. % Ni, about 20.5 wt. % Cr, about 9.0 wt. % Mo, about 5.0 wt. % Nb, and about 5.0 wt. % Fe, and
- d) binder comprises a Hadfield austenitic manganese steel.

The claims are deemed to correspond to the species listed above in the following manner:

- Claims 7, 18, 33, 56, and 73 to species a),
- Claims 8, 19, 34, 57, and 74 to species b),
- Claims 9, 20, 35, 58, and 75 to species c), and
- Claims 10, 21, 36, 59, and 76 to species d).

The following claim(s) are generic: 1-6, 11-17, 22-32, 37-55, 60-72, and 77-83.

The species listed above do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, the species lack the same or corresponding special technical features for the following reasons: the binders do not have the same or overlapping compositions.

## Continuation of B. FIELDS SEARCHED Item 3:

EAST: (boron adj2 carbide or b4c or boride or carbide or hard adj2 (material or matter or particle)) same (binder with ((ni or nickel)) with (iron or fe))) and (419/\$2.ccls. or 75/\$3.ccls.)  
hadfield adj austenitic adj manganese adj2 steel and (boron adj2 carbide or b4c or boride or carbide)